Investigation of Water Quality In The 100 Acres Quarry Area Waite Park, Stearns County, MN

July 9, 1992

By

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Stearns County Park Department
425 72nd Avenue South
St. Cloud, MN 56301
Attn: Mr. Chuck Wocken, Parks Director

Re: Report on the 100 Acre Quarry water quality study.

The week of July 6-9, 1992 was spent on the 100 Acre Quarry site examining the water quality of eight designated quarries or Pits. The PIts examined were numbers 1, 2, 3, 7, 8, 11, 13, and 18. The maps that you provided were adequate to provide access and locate each quarry site. It is my understanding that this site is under consideration for the establishment of a new County Park. Many questions have been asked about the quality of quarry water, especially if the water contains toxic substances--a liability question then surfaces. This investigation will clarify a number of important questions, and leave some unanswered until further studies evolve.

The primary purpose of this water quality investigation is to determine the suitability of the quarry water to support biological organisms. Many questions have been raised as to the potential toxicity of the quarry water due to the amount and variety of refused dumped into them over the past 100 years. The secondary purpose of this study is to establish their physical condition, chemical condition, and trophic state index. To present the actual field data several tables will be presented and individually discussed.

Quarries are unnatural waterbodies that are deep, have sheer rock walls; tiny watersheds composed of bedrock, thin soils and hardy vegetation; and essentially no shoreline or littoral zone. These waterbodies are filled with groundwater and rainwater that over time become phosphorus and nitrogen depleted making them very unproductive. They have no steady source of nutrients due to the tiny watershed and rely on rainwater for a scant nutrient supply, and snowmelt runoff in Spring.

Table 1 shows that the Summer dissolved oxygen profiles are very similar and all end with zero oxygen in deeper (hypolimnetic) waters. The oxygen demanding microorganisms, decomposing quarry sediments, create a strain on the quarry by removing life-giving dissolved oxygen in the deeper water. Examples of sediment composition are leaf litter, some eroded soils, tree fragments, human refuse, and sedimented algal and fish remains. During the Winter ice cover season I would not be surprised if several of the quarries "froze out", which is a term used by fisheries biologists for the total lack of oxygen that causes Winter fish kills. Notice the bulge or sharp increase in dissolved oxygen at the 4, 5 and 6 meter depth (3.28 ft./meter); this is caused by deep water algal photosynthes since this process is inhibited by the sunlight's ultraviolet light in the very transparent surface waters. This is a classic example of oligotrophy or "food-poor transparent lakes", such that we find in northern Minnesota Boundary Waters.

Table 2 shows the Summer temperature profiles for the quarries. Notice the sharp change in temperature at the 4 to 5 meter depth. This separates the warm surface waters or epilimnion from the cool deep bottom waters called the hypolimnion. The sharp temperature change zone is usually referred to the thermocline or "temperature curve" region or the metalimnion. These Summer profiles are typical of natural lakes.

Table 3 shows the conductivity values of the quarry water. Conductivity is the ability of the water to conduct an electric current. This is a measure of the charged ions in the water and an indirect measure of the total dissolved solids. Distilled water has a conductivity value of zero. The Mississippi River has a value of about 270, and hard well water may exceed 700. The values found in the quarries are all not typical of groundwater in the area since they are so low. This means that rainwater plays a large part in supplying the quarries with dilution water as rainwater conductivity is usually less than 20. Of particular interest is the slight increase in conductivity with depth. If the deep water conductivity values were over 500 to 1000 a special condition called meromixis could exist indicating a refuse material was deposited and is leaching out in bottom waters. This layer may not mix with the other quarry water for years, but could be anaerobic and toxic. This condition was not found in the eight quarries examined.

Table 4 shows the pH or acid/base conditions of the quarries. Values above pH 7 are called basic and values below pH 7 are called acidic. Preferred values, for normal aquatic biological life, are between pH 7 and pH 9. The quarries show typical values of soft waters, sometimes dipping a little below pH 7. These waters do not have a good buffering capacity, calcium and magnesium hardness, and may be extremely subject to acid rain. Notice Pit 7 and Pit 8 have low salts or conductivity and also the lowest pH, they have less buffering capacity.

Table 5 shows some of the water chemistry found in the quarries. The water hardness in all quarries would be classified as quite soft having a hardness of 36 to 83 mg/L as $CaCO_3$ or range from 2-5 grains hardness. Quarry 11 shows harder water that may be due to runoff from soils by a larger watershed. All quarries are extremely low in phosphorus and nitrogen which greatly limits biological production. These quarries are not good for fish production or even minnow raising for commercial use, stunted fish are often observed. Some quarries, in the area, have been used for "put-and-take" fishing where fish feeding is necessary, but on their own will not produce many fish.

Table 6 shows the visual transparency of the quarries also called the Secchi disk reading. These values greatly exceed any lake in Stearns County and are typical reading in northern Minnesota lakes and Lake Superior. The transparency depth of 10.74 meters is the greatest that I have ever observed. This great visual transparency means that algal production is low. Algal chlorophyll "a" biomass ranged from .25 to 1.66 ug/L, levels never observed in other lakes in Stearns County during Summer months. These quarries are special in this regard--an outdoor laboratory worth an historical marker.

Table 7 lists the general observations made while traveling to each quarry and during the testing period.

The section following the tables discusses the acute toxicity test.

TABLE 1.
PROFILE DATA JULY 7, 1992
DISSOLVED OXYGEN (mg/L or ppm)

DEPTH (METERS)	PIT1	PIT2	PIT3	PIT7	PIT8	PIT11	PIT13	PIT18
0	9.18	8.93	8.68	8.86	8.63	9.25	9.30	9.10
1	9.54	9.03	9.14	8.63	8.61	9.04	9.25	9.01
2	9.41	8.60	8.45	8.84	8.69	9.04	9.33	8.80
3	9.44	8.46	8.88	9.45	8.67	8.84	9.24	9.32
4	11.20	8.12	11.43	10.48	9.11	12.63	9.23	10.39
5	12.30	10.69	.21	10.66	6.35	13.44	11.13	9.50
6	9.32	12.01	0	5.89	3.78	11.82	12.02	8.46
7	7.35	10.21	0	.50	2.53	6.76	10.12	7.10
8	4.22	8.55		0	1.92	3.31	8.60	5.55
9	2.67	7.01		0	.64	.41	6.75	4.03
10	1.45	4.77		0	0	0	4.28	2.20
11	.55	1.22		0	0	0	1.85	.95
12	0	0		0			0	0
13	0	0		0			0	0
14								
15								

Note: readings only extended to the "0" mg/L dissolved oxygen depth

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TABLE 2.
PROFILE DATA JULY 7, 1992
TEMPERATURE (DEGREES CELSIUS)

DEPTH (METERS)	PIT1	PIT2	PIT3	PIT7	PIT8	PIT11	PIT13	PIT18
0	21.7	20.8	20.0	20.1	20.3	20.2	20.0	19.3
1	20.3	20.2	19.1	19.9	19.6	19.9	19.8	18.9
2	19.7	19.8	18.5	19.4	19.3	19.8	19.8	18.4
3	19.2	19.5	17.0	18.3	17.5	19.5	19.5	17.2
4	17.5	19.0	13.6	13.9	13.2	17.1	19.2	14.2
5	12.9	17.3	10.5	11.1	10.0	13.0	17.1	12.4
6	10.4	12.9	8.5	8.8	8.0	10.1	14.5	9.6
7	8.7	11.2	7.0	7.5	6.7	8.9	12.2	8.2
8	7.7	10.6	MAX	6.5	5.9	7.8	10.8	7.0
9	7.3	9.4		5.9	5.4	7.2	9.8	6.2
10	6.4	8.7		5.4	5.1	6.5	9.0	5.7
11	6.1	7.8		5.2	4.9	5.1	8.5	5.4
12	5.2	7.2		5.1	4.8	5.1	8.0	5.3
13	5.1	6.7		5.1	4.7	MAX	7.4	5.2
14	MAX	6.1		5.1	4.6		7.1	5.2
15		5.4		5.1	4.6		6.5	5.0
16		5.3		4.8	4.6		6.1	MAX
17		5.2		4.8	4.6		5.9	
18		5.1		MAX	4.5		5.7	
19		5.1			4.5		5.3	
20		4.9			4.5		MAX	
24		MAX			4.5			
30					MAX			

Note: 1 meter = 3.28 feet

TABLE 3.

PROFILE DATA JULY 7, 1992
CONDUCTIVITY (MICROMHOS/CM AT 25C)

DEPTH (METERS)	PIT1	PIT2	PIT3	PIT7	PIT8	PIT11	PIT13	PIT18
0	194	119	117	86	96	250	155	180
1	195	119	118	86	96	250	155	180
2	197	122	122	87	96	262	156	180
3	197	123	131	90	100	267	158	184
4	210	127	135	92	102	273	158	189
5	215	127	.	.	105	278	159	193
6	220	132	.	92	105	280	161	199
7	224	.	135	92	.	.	161	199
8	224	.	MAX	95	.	.	163	199
9	.	232		98	.	.	164	.
10	.	.		99	.	.	167	.
11	.	.		.	.	.	168	.
12	.	.		.	.	280	.	.
13	224	.		.	.	MAX	.	.
14	MAX	.		99	108		168	200
15		.		.	.		.	200
16		.		.	.		.	MAX
17		.		99	.		.	
18		.		MAX	.		.	
19		.			.		168	
20		232			.		MAX	
24		MAX			108			
30					MAX			

TABLE 4.

PROFILE DATA JULY 7, 1992
FIELD pH VALUE (Acid/Base Indicator)

DEPTH	PIT1	PIT2	PIT3	PIT7	PIT8	PIT11	PIT13	PIT18
SURFACE	8.30	7.66	7.61	7.30	7.33	7.89	8.33	7.49
MIDDLE	7.94	7.58	7.54	7.17	7.02	7.65	7.95	7.49
BOTTOM	7.45	7.24	7.03	6.72	6.73	8.15	7.40	7.09

TABLE 5.

SURFACE WATER DATA
WATER CHEMISTRY

QUARRY OR PIT NUMBER	HARDNESS AS CaCO3 (mg/L)	NITRATE NITROGEN (mg/L)	DISSOLVED PHOSPHORUS (ug/L or ppb)	TOTAL PHOSPHORUS (ug/L or ppb)
1	84	0	<5	<5
2	54	0	<5	<5
3	56	0	<5	<5
7	36	0	<5	<5
8	48	0	<5	<5
11	116	0	<5	8
13	70	0	<5	<5
18	82	0	<5	<5

Note: Middle and bottom samples were "0" for nitrates and <10 ug/L for both dissolved and total phosphorus. The Trophic State Index (TSI) for total phosphorus is 37.

TABLE 6.

SURFACE WATER DATA
PHYSICAL AND BIOLOGICAL DATA

QUARRY OR PIT NUMBER	SECCHI DISK TRANSPARENCY (Meters)	SECCHI DISK TROPHIC STATE INDEX	ALGAL CHLOROPHYLL A BIOMASS (ug/L)	ALGAL CHLOROPHYLL TROPHIC STATE INDEX	AVERAGE TSI
1	4.26	37	1.54	34	36
2	7.45	31	1.66	35	34
3	4.10	39	1.81	36	37
7	5.46	36	.92	30	34
8	5.42	36	1.85	36	36
11	5.96	34	1.11	31	34
13	10.74	26	.85	27	30
18	9.50	27	.25	20	28

TABLE 7.

OBSERVATIONS AT EACH PIT OR QUARRY
DURING THE SAMPLING TRIPS
JULY 6 AND 7, 1992

PIT 1: Observed sunfish, bass, and natural minnows. Considerable rock art indicates frequent use by local natives. Observed a couple fishing July 6th. A large quarry with high bluffs, very attractive site.

PIT 2: A large quarry. Cattail stand observed. Natural minnows observed. Surrounded by vegetation. While portaging between Pit 2 and Pit 1 the large shaded piles of quarry released cool air, it felt good; perhaps cooled at night and provided a microclimate daily.

PIT 3: Automobile submerged in the water, a van. A very fine, colorful, oil slick covers some of the surface area. Observed a leech swimming, frogs, minnows, and a fish that jumped, perhaps a bass.

PIT 7: Trees and vegetation surrounding the quarry. Fallen trees in the water covered with algae. Observed a frog, dead crayfish, and water beetles. Old beaver markings on trees around quarry. Juvenile woodchuck observed drinking quarry water.

PIT 8: Heavy scum of oil on the surface. It can be observed to part with a canoe stroke and close in seconds. Natural minnows observed, also several dead minnows along the shoreline. No source of the oil was observed. While portaging to Pit 8 from Pit 7, the air temperature dropped measurably while passing the granite piles--they must retain considerable coolness from nights and refrigerate the area during the day.

PIT 11: Cattails on water edge. Water depth 56 feet by depth sounder. Water beetles observed swimming in the water and vegetation all around the quarry.

PIT 13: Observed a bullhead, bass, and snails in the water. Automobile sunk in the water, a van. The depth sounder recorded 78 feet maximum depth.

PIT 18: Observed bass in the water and minnows. Numerous fallen trees in the water.

24 HOUR IN SITU ACUTE TOXICITY TEST
USING JUVENILE FATHEAD MINNOWS
JUNE 6 TO JUNE 7, 1992

DEFINITIONS: In Situ = minnows tested in natural quarry water and left in the quarry-in place. Quarry water taken into the laboratory for minnow survival study, in Latin as In Vivo. When organisms like fish are tested using well water in glass jars this test is termed In Vitro.

Acute Toxicity = Short term survival test of toxic substances affecting the survival of of living organisms. In contrast to Chronic Toxicity which is a long term study usually over the life cycle of the test organism.

Juvenile Fathead minnows (*Pimephales promelas*) were obtained from Lou's Bait Shop in St. Cloud, MN. They were transported to the 100 Acre Quarry area in plastic bags containing oxygenated water. The minnows were temperature acclimated to quarry water temperature by placing the bags in the quarry water for about 4 hours. After the acclimation period minnows were screened for physical condition and disease, and the healthiest ones were used for the test. Twenty minnows were used for each quarry test, ten per cylinder, to obtain a statistical average and percent survival.

During the acclimation waiting period an acute toxicity test apparatus was place in each of eight designated study quarries, pits 1, 2, 3, 7, 8, 11, 13, and 18. The test apparatus consisted of two one-gallon size nylon screen, closed bottom, cylinders stapled to a wood float. These were anchored to the shore and allowed to move freely two to three feet from shore. The screen allowed quarry water to circulate freely providing dissolved oxygen and some food items.

A special test apparatus was designed to be left at Lou's Bait Shop to serve as the minnow survival control. Ten minnows were placed into each of two cylinders and the apparatus was submerged in the original source water used to keep the minnows. The dissolved oxygen of the water was 6.45 mg/L, pH 7.11, conductivity 750 umhos/cm, and temperature 12.7 C. This water was cooler than the quarry water but will serve as a good minnow survival control since equipment was not available to hold the water at 20 C, or general quarry temperature. On July 7th and July 8 the minnows were observed and all 20 were alive at the Bait Shop. This indicates that the minnows were in good condition and will serve as test organisms.

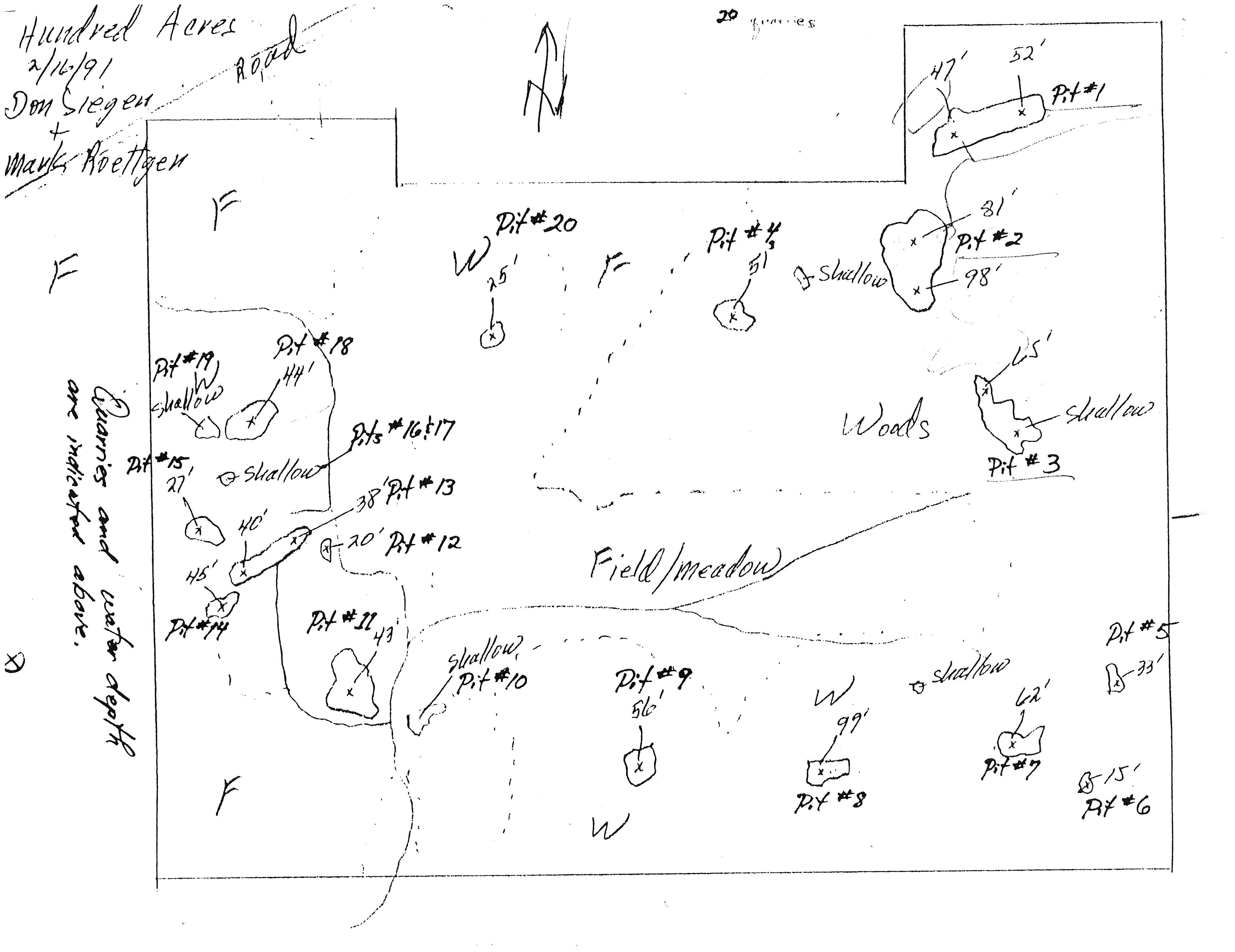
TABLE 8.

SURFACE WATER ACUTE TOXICITY TEST

PIT	Minnow Survival Cylinder one	two	TOTAL SURVIVAL	Percent Survival
1	10	9	19	95
2	10	10	20	100
3	10	10	20	100
7	10	10	20	100
8	10	10	20	100
11	10	10	20	100
13	10	10	20	100
18	10	10	20	100

Based on these statistics of 95-100% survival for the 24 hour SURFACE WATER acute toxicity test it is my observation that high concentrations of toxic metals, and other substances do not exist in the surface water of the eight pits examined. This is confirmed by the new observation of minnows and larger fish in all quarries except Pit 7, where no fish were observed. The small fish populations now existing in the quarries may be suffering from chronic exposure to toxic substances in very low concentrations that inhibit their ability to reproduce. This of course, is unknown at this time. The potential source of toxic substances would be the refuse dumped into the quarries like automobiles. Automobile parts with chromium, copper, zinc, asbestos, grease and oils; quarry mining wastes, like lubricating oils and slag from cable rock cutting; and refrigerators are reported to have been dumped into the quarries which may contain PCB's. An examination of the fish, particularly the female, to determine egg production success will be of interest in further studies. No fish fry were observed during our visit to confirm reproduction of the indigenous populations. However, we may have seen some juvenile minnows at Pit 18 but were unable to capture them for observation.

Cool hypolimnetic waters, from each quarry, were aerated in the laboratory in gallon glass jars and maintained at 13 C, the same temperature as the Bait Shop minnow holding basins. Minnows were placed into the jars In Vivo for 24 hours. No acute toxicity was observed during this period since 100% survival was observed using hypolimnetic water. This indicates that high concentrations of potential toxic substances, metals, etc., were not released into the anaerobic deep hypolimnetic waters from the sediments. In all quarries, except Pit 8, no toxic hydrogen sulfide gas (rotten egg gas) smell was noted from deep anaerobic (absence of oxygen) hypolimnetic waters. This dissolved gas is toxic to fish. In Pit 8 only, a slight hydrogen sulfide smell, was noted. This was the quarry with the heavy oil scum and the sulfides may come directly from the oil or indirectly by sulfate reducing bacteria. The oil scum will reduce sunlight and algal photosynthesis (oxygen production) causing the quarry water to become anaerobic. Sulfate ions, under anaerobic conditions, are transformed into Hydrogen sulfide by sulfur bacteria. These quarries, with their diluted groundwater, would be expected to have low concentrations of sulfate ions, as the near absence of dissolved hydrogen sulfide gas indicates.



Quarries and water depth are indicated above.